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I. GENERAL INTRODUCTION

In the last quarterly progress report we indicated the initiation of an investigation on the identity and properties of native defects in CdTe. During the present reporting period we have continued this study.

Electrical transport measurements were conducted with the cooperation of Dr. H. H. Woodbury. In the course of studying the electrical properties of high-purity single crystals of CdTe, a new center, thought to be a native double acceptor, has been observed. It is believed to be the first of its kind in compound semiconductors identified by electrical transport measurements. This center is formed during heat treatment in a Cd atmosphere. The doubly ionized acceptor level lies 0.056 ev below the conduction band and when this level is filled the center contains two electrons and is an effective hole trap at low temperatures. In fact, the singly negatively-charged center has such a low cross section for electron capture that it is impossible to observe a normal freeze out of electrons into the second level when the samples are cooled below a critical temperature region. Details of this work are presented in the form of a publication draft to Physical Review Letters in Section II.

Another approach toward the identification of point defects is the technique of electron paramagnetic resonance. In cooperation with Dr. G. W. Ludwig we have studied n-type CdTe by this

method. Two resonance lines have been observed so far. A line with a g value of 1.68 is believed to be due to shallow donor impurities. The exact defects responsible for it are not yet known. Further work is planned to learn their identity. The other resonance line was observed with a g value of 2 and the line has been associated with the Cr^+ ion in a cadmium site. Details of this study are given in Section III.

We have also continued to examine fluorescent emission spectra in the zone-refined CdTe and in CdTe subjected to various heat treatments. Some data has been taken with samples immersed in He. Of current interest is the possibility of correlating the 1.54 ev emission in CdTe (believed analogous with the "green edge emission" of CdS) with transitions between the -2 charged double acceptor level described in this report and the valence band. The energy differences and several other aspects of the correlation appear favorable. Unresolved problems exist in accounting for details such as the origin and temperature dependence of the doublet structure, and correlation with analogous spectra of other II-VI compounds. Further experiments are currently in progress.

II. A DOUBLE ACCEPTOR DEFECT IN CdTe*

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purity single crystals of CdTe, a new center, thought to be a
native double acceptor, has been observed. It is believed to be
the first of its kind in compound semiconductors identified by
electrical transport measurements. This center is formed during
heat treatment in a Cd atmosphere. The doubly ionized acceptor
level lies 0.056 ev below the conduction band and when this level
is filled the center contains two electrons and is an effective
hole trap at low temperatures. In fact, the singly negatively-
charged center has such a low cross section for electron capture
that it is impossible to observe a normal freeze out of electrons
into the second level when the samples are cooled below a critical
temperature region. A similar level about 0.09 ev below the
conduction band has also been found in CdS.

CdTe samples were prepared by techniques already described.[1]
High-purity crystals having a residual impurity donor concentration
of about 10^{15} cm^{-3} were used.[2] Hall bars of approximately
3 x 3 x 10 mm^3 were sealed in small evacuated quartz ampoules to
which Cd metal was added. These were heated to various temperatures
for varying lengths of time and then quenched. The surface
regions of the samples were removed by grinding, etching, and a

final chemical polish. The crystals were then studied using
conventional d.c. techniques to measure the Hall coefficient,
resistivity, and Hall mobility from $350^{\circ}K$ to $12^{\circ}K$. There were
provisions for exciting the samples with a small incandescent
lamp mounted inside the cryostat.

The temperature dependence of the Hall constant for electrons
in several samples is shown in Fig. 1. Curve A represents an
unfired sample; curve B, a sample fired at $900^{\circ}C$ for 30 min.; and
curve C, a sample fired at $900^{\circ}C$ for 285 hrs. The solid curves
correspond to measurements without light and the dotted curves
show the effects following photoexcitation at the lowest tempera-
ture. Freeze out of electrons into the level of interest starts
near $300^{\circ}K$ and is most pronounced in curve B. The thermal
activation energy is 0.056 ev. At about $110^{\circ}K$ the electronic
equilibrium starts to lag the thermal equilibrium. The lag
increases as the temperature is lowered and at $85^{\circ}K$ it is
necessary to wait several hours to establish electronic equilibrium.
At lower temperatures it becomes impossible to reach equilibrium
with regard to the 0.056 ev level. This sluggishness was
observed for the heating as well as the cooling of samples in
this temperature region.

The peculiarity of the above behavior suggests that a barrier
is associated with the 0.056 ev level. The decay of conduction
electrons following photoexcitation was measured at four tempera-
tures in the critical temperature region, i.e., 95 to $115^{\circ}K$. The
simple relation $\Delta n = c \exp(-t/\tau)$ was observed over three decades
at each temperature and over the limited temperature region the
lifetime can be expressed as $\tau = \tau_o \exp(0.27 \text{ ev}/kT)$, where
$\tau_o = 3.2 \times 10^{-12}$ sec.

In Fig. 2 the Hall mobilities are shown corresponding to the Hall constants of Fig. 1. Curve A again is the unfired sample which also exhibits the intrinsic mobility over the range shown.[2] Photoexcitation did not change the mobility for this sample. There is, however, a pronounced effect on the mobility of the fired samples, as seen from the dashed curves. After photoexcitation at the lowest temperature, the mobility shows a marked increase. The original mobility curve is rejoined at about $100^\circ K$, the temperature at which the excess electrons, thrown out of equilibrium at the lowest temperature, are able to freeze into the 0.056 ev level.

We conclude that the 0.056 ev level, although close to the conduction band, is the doubly ionized state of a two-level acceptor defect. The singly ionized state has a charge of (-1) and is responsible for the barrier observed. Photoexcitation at the lowest temperature produces hole-electron pairs. The holes are captured (trapped) by the filled double acceptor centers resulting in a change of the charge state of the centers from (-2) to (-1). The excess electrons are unable to reach electronic equilibrium with the centers because of insufficient kinetic energy to surmount the barrier about the singly occupied defect. When the temperature is raised to the critical region, the Hall constant increases and the mobility decreases to their original values as electronic equilibrium is re-established.

The explanation of the behavior observed in these crystals is based on a double acceptor model analogous to that established for many impurities in Ge.[3] Qualitatively, the observed effects on mobility and Hall coefficient with and without light show a one-to-one correspondence between the effects reported here and those reported, for example, for Mn-doped Ge.[4] A quantitative

difference appears to be that in the present case, the ratio of the barrier to the second (thermal) ionization energy is much greater than the ratio seen for double acceptors in Ge. This prevents thermal equilibrium from being established as the CdTe samples are cooled but causes no difficulty for the double acceptor centers seen in Ge.

It is to be emphasized that the double acceptor centers described here are not necessarily the dominant defects in the CdTe system. Under the present preparative conditions their formation is accompanied with a concurrent formation of donor centers. The results indicate that for short firing times the samples are slightly more n-type than they were originally but are also more compensated. Hence, the 0.056 ev level appears to be dominant. After long periods of firing the concentration of both acceptor and donor defects increase, but the latter more than the former. There is an additional peculiarity in this system. Short firing times of about one-half hour produce, after surface region removal, a homogeneously-changed sample. Long firing times of several hundred hours also yield homogeneous samples. However, treatment times of intermediate periods result in inhomogeneous crystals. This suggests that at least two processes occur during heat treatment. The fast one is essentially complete after a short time and then is succeeded by a much slower process.

The following evidence strongly suggests that the double acceptor center described here is a native defect. It is observed only when samples were quenched and is seen in excess of the number of donors and acceptors normally found in slow cooled or annealed samples. Spectroscopic analysis on CdTe has revealed that likely common metal impurities are below the defect

concentrations observed. After heat treatment in excess Cd, a similar double acceptor defect with the doubly ionized level 0.09 ev below the conduction band has also been seen in CdS. Its electrical properties are identical to the center described here in CdTe. Furthermore, CdTe samples showing the behavior illustrated in curve B of Fig. 1 go to high resistance within several days on standing at room temperature. This decay is suggestive of recombination of Frenckel defects or precipitation of Schottky centers. The present results, however, do not permit an unambiguous identification of the native double acceptor center. Although we believe that the center is a simple native defect, we cannot rule out the possibility that the actual defects involved may be complexes of interstitials and/or vacancies or even chemical impurities that are not normally electrically active. However, such complexes must maintain the properties of a double acceptor.

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1. M. R. Lorenz and R. E. Halsted, J. Electrochem. Soc., April 1963 (to be published).

2. B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev., March 15, 1963 (to be published).

3. See, for example, W. W. Tyler and H. H. Woodbury, Phys. Rev. 102, 647 (1956).

4. Compare Figs. 11 and 10 of Ref. 3 with Figs. 1 and 2, respectively, of this letter.

FIGURE CAPTIONS

Fig. 1.   The temperature dependence of the Hall coefficient, R_H, of n-type CdTe samples. The dashed curves show R_H after photoexcitation at the lowest temperature.
A - original high-purity material.
B - Cd fired for one-half hour at $900^{\circ}C$.
C - Cd fired for 285 hours at $900^{\circ}C$.

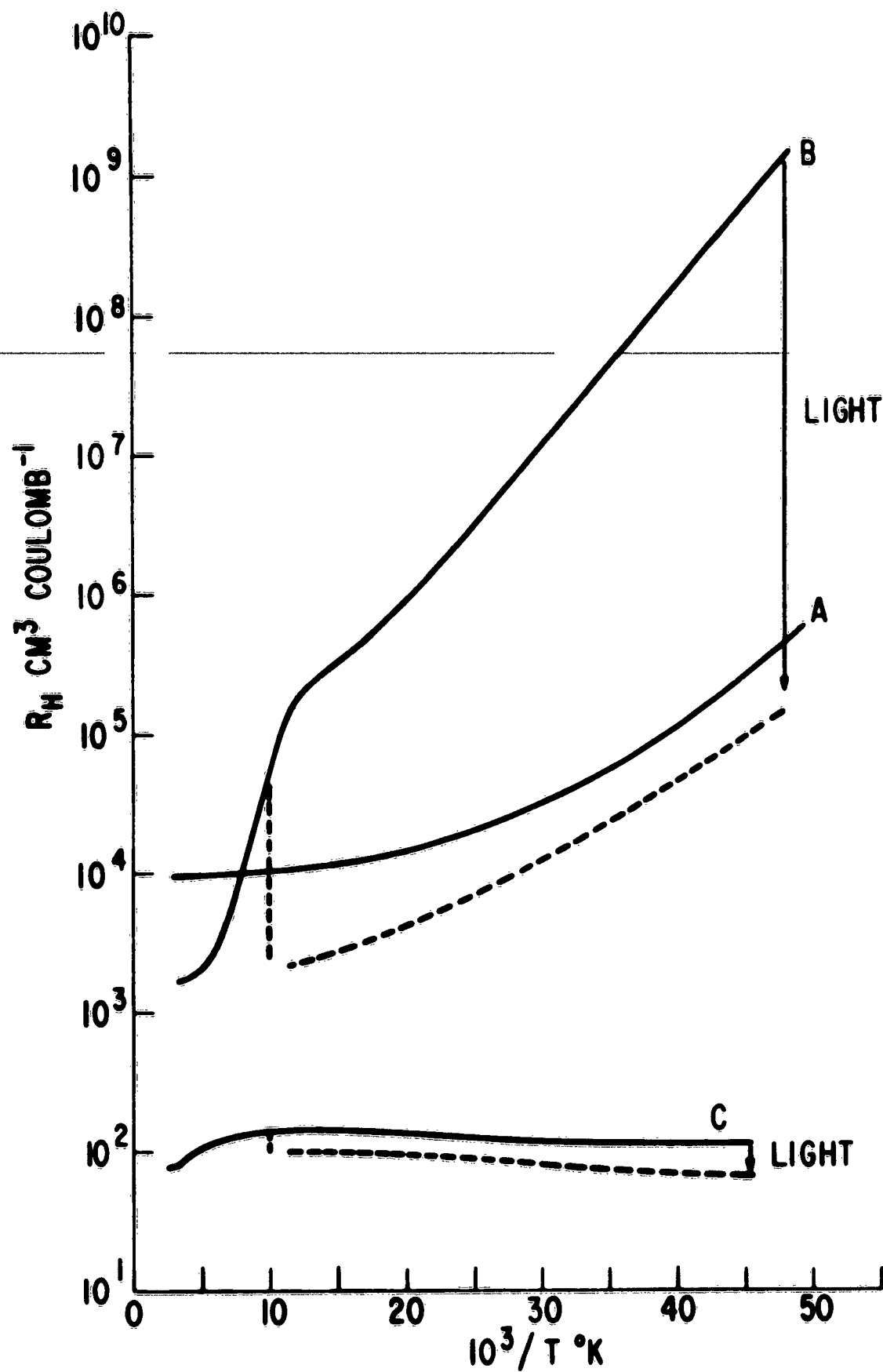Fig. 2.   The electron Hall mobility, μ_H, of the samples shown in Fig. 1.
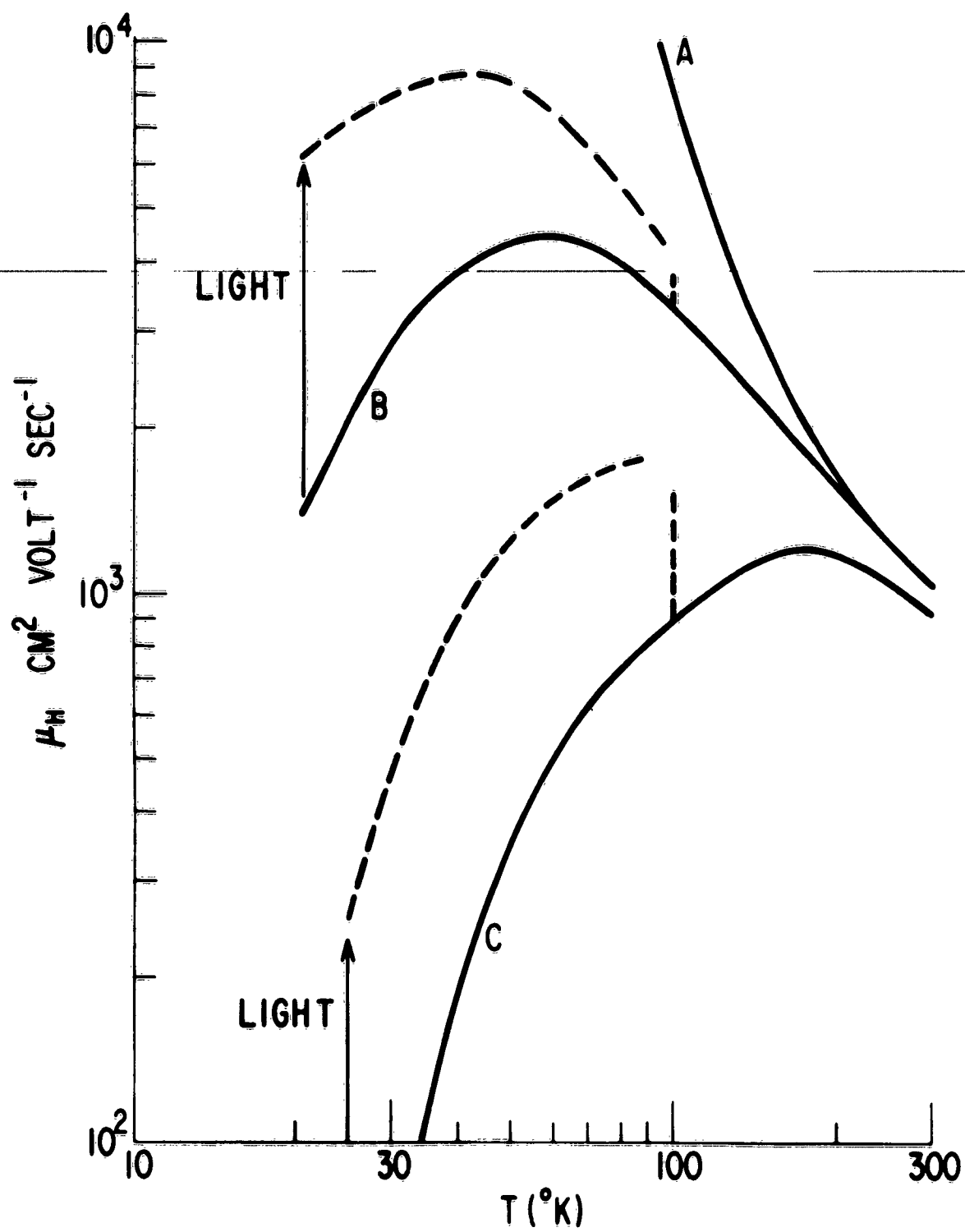
Fig. 1

Fig. 2

III. PARAMAGNETIC RESONANCE IN CdTe - G. W. Ludwig and M. R. Lorenz

The technique of electron paramagnetic resonance has been utilized relatively little for the study of defect centers in II-VI compounds. In CdTe the only centers for which such data appears in the literature[1] are the transition metal impurity ions Mn^{2+} and Co^{2+}. We have initiated a program of study of paramagnetic resonance in CdTe, hoping to correlate such measurements with data from other techniques, notably Hall coefficient and resistivity studies. Thus far, we have tentatively associated a resonance line at g = 1.68 with shallow donor impurities (not yet further identified). We have also studied the spectrum of the impurity ion Cr^+, which will now be discussed in somewhat greater detail.

When CdTe crystals are chemically polished with a dichromate-sulfuric acid solution, they retain an adsorbed layer of presumably dichromate ions. The most thorough rinsing with triple distilled water fails to remove this layer completely. When samples "cleaned" this way are heat treated in a Cd atmosphere, they become Cr doped and give rise to paramagnetic resonance absorption in the vicinity of g = 2. If the magnetic field H is restrained to be in the (110) plane, the spectrum is simplest for H in a zero cubic field splitting direction (see Fig. la). There it consists of a pattern of lines having an envelope of intensities. The pattern is consistent with assigning the structure to hyperfine interaction with the magnetic isotopes Cd^{111} and Cd^{113} occupying twelve essentially equivalent sites, the mean hyperfine interaction being $\sim 5 \times 10^{-4}$ cm^{-1}.

As the magnetic field is rotated toward the [001] direction, each of the hyperfine lines splits, it being clear that there are

at least three fine structure components $(S \geq 3/2)$. Actually, one would guess that five fine structure components are present in all $(S = 5/2)$, since the fine structure splitting vanishes in a purely tetrahedral crystalline field for $S \leq 3/2$. Cr^+ is an impurity which would be expected to have a half-filled $3d$ shell and $S = 5/2$. Therefore, a crystal containing chromium enriched in the isotope Cr^{53} was prepared. Indeed a spectrum (see Fig. 1b) similar to that of Fig. 1a except for the presence of Cr^{53} hyperfine structure, was detected. This sample was then examined by the electron-nuclear double resonance technique of Feher.[2] The spin-Hamiltonian which we deduce for Cr^+ in CdTe is
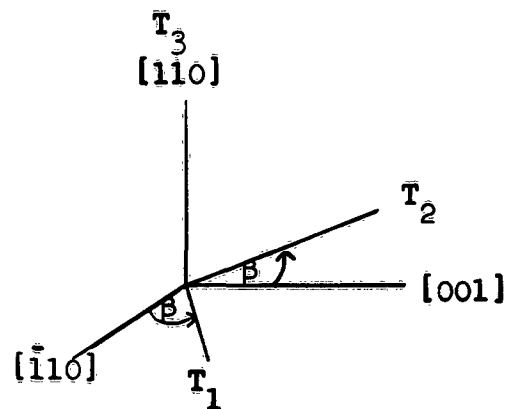
$$\mathcal{H} = g\beta S \cdot H + \frac{a}{6} [S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1)]$$

$$+ AS \cdot I - \gamma\beta_n H \cdot I$$

$$+ \Sigma_k (S \cdot T_k \cdot I_k - \gamma\beta_n H \cdot I_k)$$

with the parameters shown below:

$S = 5/2$

$g = 1.9997 \pm 0.0002$

$|a| = (3.1 \pm 0.6) \times 10^{-4} \text{ cm}^{-1}$

$A = (12.781 \pm 0.005) \times 10^{-4} \text{ cm}^{-1}$ } for Cr^{53}

$\gamma = 0.3161 \pm 0.0008$

$T_1 = (5.82 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$

$T_2 = (5.63 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$ } for Cd^{113}

$T_3 = (5.61 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$

$\beta = 37 \pm 5^0$

The paramagnetic resonance transitions for such a spin-Hamiltonian have been discussed previously and lead to the quoted value of $|a|$.

The ENDOR transitions of Cr^{53} are given by

$$hf = |AM - [S(S + 1) + (2m - 1)M - M^2] (A^2/2h\nu) - \gamma\beta_n H|$$

Such transitions were detected for $M = \pm 1/2, \pm 3/2$ and $- 5/2$; from their analysis one obtains the quoted value of A, a value for γ in good agreement with published values for Cr^{53}, and confirmation of the spin $S = 5/2$. ENDOR transitions of Cd^{111} and Cd^{113} were detected with good signal-to-noise only for H in a [110] direction. From their analysis one obtains the parameters given above describing the hyperfine interaction with Cd^{113}.

We conclude that we have identified paramagnetic resonance of Cr^+ in CdTe. The hyperfine interaction with twelve equivalent Cd neighbors leads us to believe that the Cr^+ substitutes for Cd, leading to twelve nearest Cd neighbors; substitution for Te would lead to four nearest Cd neighbors. The resonance parameters are similar to those reported recently by R. S. Title[3] for Cr^+ in ZnS.

REFERENCES

1. G. W. Ludwig and H. H. Woodbury, Solid State Physics 13, 223 (1962).

2. G. Feher, Phys. Rev. 114, 1219 (1959).

3. R. S. Title, Bull. Am. Phys. Soc. Ser. II 8, 23 (1963).

FIGURE CAPTION

Fig. 1.   Spectrum of $Cr(3d^5)$ in CdTe at 4.2°K with the
spectrometer tuned to dispersion under rapid
passage conditions.

a) H in the zero cubic field splitting
direction (p = 0).

b) H in a [001] direction.

SPECTRUM OF Cr⁺ IN CdTe

→| 34 GAUSS |←
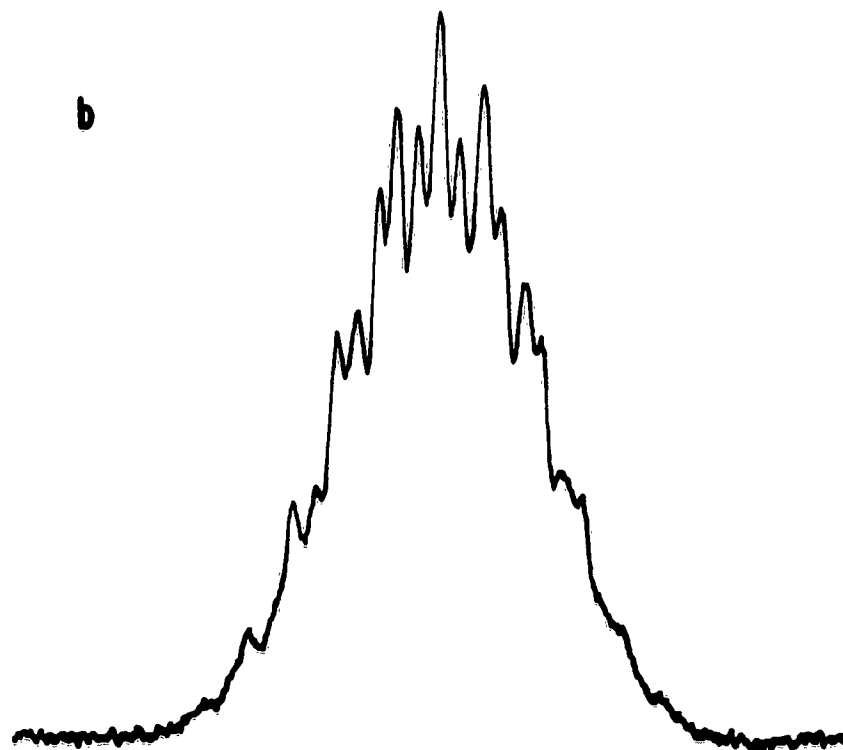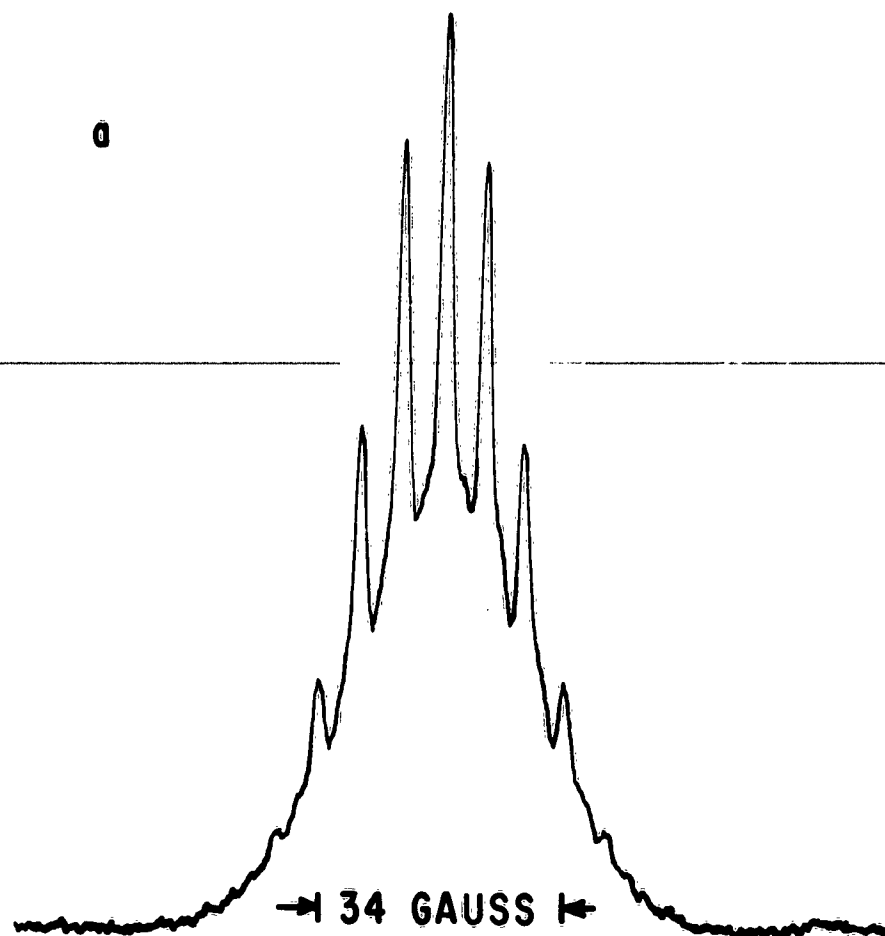
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